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(54) STABILIZATION OF AQUEOUS SOLUTIONS OF BROMINE

(71) We, MINES DE POTASSE D'ALSACE S.A. a French body corporate of 11 Avenue d'Altkirch, 68 Mulhouse, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to methods of and compositions for stabilizing bromine in aqueous solution. The invention provides both methods and compositions for doing this, including particularly solid compositions which contain as their main component a compound which will release bromine under the action of an oxidising agent when brought into contact with water and which contain a sufficient amount of a compound which decreases the rate of loss of the thus-released bromine.

It is known that bromine is used for the treatment of water such as swimming pool water, disinfection circuits of refrigeration water and so on, owing to its bactericidal and algicidal properties. For the disinfection of swimming pools, water treated with bromine moreover has the advantage of not giving off an unpleasant odour (as is the case with chlorine) and of being non-irritating to the mucous membranes, which notably improves the comfort of the bathers.

In this application, bromine is mostly used as a highly diluted aqueous solution by controlling the introduction of this solution according to the requirements of the water to be treated. However, the use of bromine in such a way can in certain cases present some difficulties since it necessitates the storage and transport of liquid bromine. For small-sized installations, for example, it is not always possible to provide premises in which the safety regulations regarding the storage and handling of liquid bromine can be met. In other cases, where the sources of bromine are not in the vicinity, it is the supply of the disinfecting agent which can raise a problem.

Bromine can also be used in the form of an organic N-brominated compound, but these compounds are only very slightly soluble in water; the quantity of bromine which is actually released in the water is thus much more difficult to regulate and the control of bactericidal effectiveness is then a particularly delicate operation.

For the above reasons an indirect method of sterilising by bromine is sometimes used, in which bromine is given up by a bromide, preferably an alkalimetal bromide. In this indirect method, the bromine is oxidised *in situ* by an oxidising agent, such as an N-chlorinated compound, chlorine water or a hypoclorite, the most frequently used one being sodium hypochlorite, for example as Javel water.

In both the direct and indirect methods of sterilisation by means of bromine, as described above, the bactericidal action seems to be due to the oxidising action of the hypobromite. Thus in aqueous solution, bromine is submitted to hydrolysis a according to reversible equation:

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr \quad (1)$$

The hypobromous acid dissociates into hypobromite ions BrO^- and into H^+ according to the equation:

$$HOBr \rightleftharpoons H^+ + BrO^- \quad (2)$$

In the case of indirect sterilisation, for example when oxidation of an alkali metal bromide by an hypochlorite is used, the reaction of the formation of the hypobromite is the following:

$$Br^- + ClO^- \rightarrow BrO^- + Cl^- \quad (3)$$

The hypobromite ions from reaction (2) or (3) act as oxidising agents according to the equation:

$$BrO^- \rightarrow Br^- + O \quad (4)$$

In practice, it has been noticed that under conditions of strong or even medium lighting such as can exist with open air swimming pools for example, the hypobromite rapidly decomposes, which results in an increase in the bromine used to obtain an equal bactericidal effectiveness. It is as if part of the bromine added directly or as bromide was lost in the water without its oxidising action having had time to produce its bactericidal effect. By way of example, with water containing initially 1.5 mg/l of bromine (calculated as active bromine) introduced as a bromine solution, it has been found that the amount of residual bromine dropped within 2 hours down to 1.035 mg/l in the shade, to 0.39 mg/l in cloudy weather and to zero under bright sunlight.

With the indirect sterilisation method, the bromide ions have a tendency to slow down the decomposition of hypobromite according to reaction (4) and thereby, to decrease the rate of loss of the bromine. This rate is nevertheless still too high to guarantee a sufficient germicidal action without an excessive use of bromine. By way of example, for a water containing 150 mg/l of sodium bromide and into which an oxidising agent is introduced in such a quantity that the starting bromine content is 1.5 mg/l, the experiments in cloudy weather showed that the bromine had completely disappeared within 6 hours, as compared to 4 hours with bromine used as a solution.

The present applicants have tried to deal with this drawback and have found a simple yet efficient method which significantly decreases the rate of loss of bromine in aqueous solutions, whatever may be the method of introducing bromine into these solutions.

The method of the present invention for the stabilization of bromine in an aqueous solution is characterised by the fact that dimethyl-5,5-hydantoin is used as a stabilising agent.

It has indeed been found that the addition of dimethyl-5,5-hydantoin allows for a significant decrease in the rate of loss of the bromine without decreasing the bactericidal action due to bromine.

When direct sterilisation by bromine is performed, dimethyl-hydantoin can be introduced into the bromine storage vessels. Preferably the dimethylhydantoin is added at some point along the circuit of production of the brominated aqueous solution. In the case of swimming pool water, for example, where a brominated aqueous solution sufficiently diluted to be introduced directly into the water to be treated is prepared according to requirements, dimethylhydantoin can also be added directly into the pool, either at regularly spaced intervals or according to the injection of the brominated aqueous solution.

As a general rule for the sterilisation of swimming pool water, bromine is used in amounts of not more than 5 mg/l, for example 0.1—3 mg/l. In order that these solutions should retain their bactericidal effectiveness during a sufficient time, it has been found that it was necessary to use an amount of dimethylhydantoin of between 5 and 60 mg/l, preferably between 10 and 40 mg/l. It is, of course, possible to use higher quantities of stabilising agent but in such cases the cost of the treatment increases without any appreciable further improvement in the rate of loss of the bromine.

When sterilisation is performed by the indirect method, there is mostly used a solid composition in which the bromine source is a bromide.

The present invention also provides solid compositions containing as their main component a compound which is able to release bromine under the action of an oxidising agent when in contact with water, and a sufficient amount of a compound which decreases the rate of loss of thus-released bromine.

In such compositions, the compound which decreases the bromine loss is dimethylhydantoin and the brominated component used is a bromide, preferably an alkali metal bromide, such as potassium bromide or in particular sodium bromide.

In such compositions, it has been found that a proportion of dimethylhydantoin which is less than 50% by weight and is, for example, comprised between 20% and 40%. gives particularly satisfactory results.

The preparation of these solid compositions presents no difficulty. The incorporation of the stabilising agent can be performed by any suitable method of mixing two solids, in particular by the tabletting method which brings the solid composition into a directly useful form.

The following examples will help in a better understanding of the invention.

Example 1.

This example shows the stabilising effect of dimethylhydantoin on the rate of loss of bromine in aqueous solution under relatively mild storage conditions.

For these experiments distilled water was used, buffered at a pH of 7.5 by the addition of sodium carbonate, in crystallizers having a capacity of 3 litres. There was first poured 2 litres of water, then the stabilising agent (except in the comparison tests) in measured quantities and lastly the titrated bromine solution in order to obtain a final concentration of 1.5 mg/l. The variation in bromine content with time was then followed, the titration method chosen being the orthotolidine colorimetric method.

This method relies on the fact that in the presence of bromine, after the addition of orthotolidine in an acid medium, there is

obtained a yellow solution with a maximum absorbtion at 4350 Å. The operating conditions were as follows: 10 ml of reagent, constituted by 1 gm orthotolidine dissolved in 1000 ml of a 10% HCl solution, were added to 1 litre of the water to be analysed, the liquid was agitated and reading was performed on a spectrophotometer within the 3 minutes which followed the addition of the reagent. The bromine content was then calculated by comparison with a calibrated curve previously set out with solutions having a known bromine content.

The crystallisers were placed side by side, in the open air, in cloudy weather, the temperature varying between 20° and 24° C. The results of this experiment are shown in the following table:—

Time in hours and minutes	Bromine content (mg/l) of the solution	
	Comparison (no dimethylhydantoin)	Test with dimethylhydantoin (30 mg/l)
0	1.50	1.50
0.30	0.840	1.030
1	0.700	0.940
1.30	0.480	0.860
2	0.250	0.800
2.30	0.100	0.660
3	0.025	0.600
4	0	0.450

This table shows that the bromine had completely disappeared from the solution within 4 hours in the absence of stabilising agent. On the contrary, with 30 mg/l of stabilising agent, the water still contained 0.45 mg/l bromine, which is a value frequently chosen for a good sterilisation of water.

Example 2.

More drastic experiments were carried out in sunny weather, the temperature varying between 20° and 22° C, all other conditions being identical to those of the preceding example. The variation of the bromine content with time was followed, both in the absence of stabilising agent and also in the presence of 10 and 50 mg/l of dimethylhydantoin.

Time in hours and minutes	Bromine content (mg/l) of the solution		
	Comparison (no dimethyl-hydantoin)	Tests with dimethylhydantoin	
		10 mg/l	50 mg/l
0	1.5	1.5	1.5
0.30	0.575	0.800	0.810
1	0.275	0.630	0.600
1.30	0.070	0.530	0.525
2	0	0.320	0.400
3		0.200	0.275
3.30		0.140	0.220
4		0.075	0.170
5		0.025	0.100

Example 3.

The experiments of this example show the stabilising action of dimethylhydantoin not on bromine in aqueous solution but on bromine in the presence of sodium bromide dissolved in water. The weather was sunny during the experiments and the temperature remained at 18° C.

Time in hours and minutes	Bromine Content (mg/l of the solution)	
	No dimethylhydantoin 150 mg/l of BrNa	150 mg/l of BrNa + 30 mg/l of dimethyl-hydantoin
0	1.5	1.5
0.30	0.620	0.800
1	0.320	0.630
1.30	0.210	0.575
2	0.140	0.530
3	0.045	0.430
4	0	0.365
5		0.275
6		0.160

WHAT WE CLAIM IS:—

1. A method of stabilising bromine in aqueous solution which comprises including dimethyl-5,5-hydantoin in the solution as stabilising agent.

2. A method according to claim 1, wherein the solution has an active bromine content of not more than 5 mg/l and the quantity of dimethyl-5,5-hydantoin used is between 5 and 60 mg/l.

3. A method according to claim 2, wherein the quantity of dimethyl-5,5-hydantoin used is between 10 and 40 mg/l.

4. A method of stabilising bromine as claimed in claim 1 substantially as herein described.

5. A solid composition containing as its main component a compound which will release bromine when in contact with water under the action of an oxidising agent, together with a stabilising agent constituted by dimethyl-5,5-hydantoin.

6. A composition according to claim 5, wherein the bromine-releasing compound is a bromide.

7. A composition according to claim 6, wherein the bromide is an alkali-metal bromide.

8. A composition according to any of claims 5 to 7, wherein the proportion of stabilising agent is less than 50% by weight.

9. A composition according to claim 8, wherein the proportion of stabilising agent is between 20% and 40% by weight.

10. A solid composition as claimed in claim 5, substantially as herein described.

11. A process for the sterilisation of water with bromine wherein the bromine is stabilised by the addition of dimethyl-5,5-hydantoin to the water.

12. A process for the sterilisation of water which comprises adding to it a solid composition according to any of claims 5 to 10 in the presence of an oxidising agent.

13. A process for the sterilisation of water as claimed in claim 11 or claim 12 substantially as herein described.

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